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(54) METHOD FOR PREPARATION OF POLYMERS CONTAINING AROMATIC AMINO GROUPS IN THE SIDE CHAIN

(71) We, CESKOSLOVENSKA AKADEMIE VED, a Czechoslovak Corporation, of No. 3 Národni, Praha 1, Czechoslovakia, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method for the preparation of polymers containing aromatic amino groups in their side chain.

The versatile reactivity of primary aromatic amino groups has developed an interest in polymers containing these amino groups, which polymers can be the starting material for numerous technically important materials. Such polymers may be suitably modified by polymer-analogous reactions of this functional group.

A number of polymeric compounds is known, which contain the primary aromatic amino groups in their structure. Aniline-formaldehyde resins formed by condensation of aniline with formaldehyde are unsuitable for further chemical transformations, because of their considerable sensitivity to hydrolysis. The same disadvantage exists to some extent also in the derivatives of polysaccharides, e.g. cellulose, where the residue containing primary aromatic amino group—formed by reduction of the corresponding polymeric nitro derivative—is linked by an ester or ether bond. Some other polymeric aromatic amino compounds have also been prepared via polymeric nitro compounds by reduction of copolymeric nitroaromatic derivatives of unsaturated acids, e.g. nitroanilide of acrylic acid. Also amino derivatives of styrene have been prepared by reduction of the corresponding nitro compounds.

Compounds of this type cannot generally be prepared by a free-radical polymerization of monomers already containing free aromatic amino groups, because this group is noted for its strong inhibition activity. This fact considerably complicates the preparation of polymers from monomers containing aromatic nitro groups by free-radical polymerization. The preparation of polymers containing aromating amino groups by some polymer-analogous reactions, e.g. by reduction of nitro-group, is usually not quantitative and often gives only poorly defined products.

According to the invention there is provided a method for producing a polymer which contains primary aromatic amino groups, wherein a monomer of a general formula I:

$$R^2\text{—NH—Ar}[\text{—O—CH}_2\text{—CH}_2]_x\text{—O—CO—}\underset{\substack{| \\ R^1}}{\text{C}}\text{=CH}_2$$

where R^1=H or CH_3, Ar is a bivalent aromatic residue, R^2 is acyl, carboxyalkyl or sulphonyl group and x is 0 to 20 is polymerized alone or copolymerized with a comonomer which is selected from acrylic or methacrylic acid or a compound derived therefrom, styrene or its derivatives, butadiene, isoprene, or with a mixture of two or more of these monomers; and the polymer is subsequently subjected to the elimination of the R^2 group by reaction with an acid or base.

The elimination of the R^2 group results in the formation of an unsubstituted aromatic amino group in the side chain of the polymer. These polymers have a wide variety of physical and chemical properties and can be prepared in this economically advantageous way with high reproducibility.

Those copolymers, which have a hydro-

philic character and, after swelling in water enable the access of hydrolytic and other agents which would otherwise affect only aromatic amine groups at the very surface, have a very important position among the above mentioned copolymers, because of the easy elimination of the R^2 group and consequential formation of the amino group and further chemical transformation thereof. Therefore, preferably the comonomer is an acrylic or methacrylic ester, which contains one or more free hydroxy groups in its alcohol residue, e.g. esters of glycols, polyglycols, glycerol, and the like. The copolymer may also be acrylamide, methacrylamide, an N-substituted acrylamide or methacrylamide, an N-substituted or unsubstituted aminoalkyl-acrylate or methacrylate, or even free acrylic or methacrylic acid.

The given types of copolymers may be prepared also in a three-dimensional cross-linked form, when monomers with two or more polymerizable bonds are used as one component of the copolymerization mixture, for instance, entirely acrylated or methacrylated glycol esters or esters of polyhydroxy compounds, methylene bisacrylamide, divinyl benzene, and the like.

A special case of a three-dimensional polymerization is the preparation of heterogeneous macroporous materials which are formed at the copolymerization of the aforesaid monomers in the presence of polymer solvents or precipitants. Separation of phases takes place in the course of the reaction and the polymerization proceeds by the heterogeneous mechanism, particularly in the later stage. The resulting material has a large inner surface (as high as several hundreds m^2/g) and a permanent porosity. The three-dimensional heterogeneous polymerization in a disperse medium is of particular technical interest, because the porous material results in a form of globular particles, which find broad application especially in chromatographic techniques and in ion exchange operations.

Embodiments of the invention will now be described with reference to the following, non-limiting Examples.

EXAMPLE 1

A solution consisting of 1 part of 2-(p-acetaminophenoxy)-ethyl methacrylate, 20 parts of 2-(β-hydroxyethoxy)ethyl methacrylate and 1 part of azobisisobutyronitrile in 100 parts of ethanol was heated to 75°C for 10 hours. To hydrolyze the copolymer formed, the solution was heated after addition of 1 part of sodium hydroxide dissolved in 1 part of water at the same temperature for another hour. The polymer, with practically all amide groups already saponified and ester functions remaining untouched at the same time, may be isolated from the solution by precipitation with ether.

EXAMPLE 2

A solution consisting of 1 part of p-acetaminophenyl methacrylate, 10 parts of acrylamide and 1 part of dibenzoyl peroxide in 70 parts of carbon tetrachloride was heated under reflux and vigorous stirring. The copolymer started to precipitate after several minutes and the polymerization was almost completed after only one hour. The white powdered copolymer was then sucked off, washed with carbon tetrachloride and dried. Total cleavage of acetyl groups took place by saponification with boiling 2% sodium hydroxide, however, a part of amide groups of acrylamide was also hydrolyzed at the same time, so that the resulting product can be characterized as the copolymer of acrylamide, acrylic acid and p-aminophenyl methacrylate.

EXAMPLE 3

A mixture consisting of 66 parts of 2-hydroxyethyl methacrylate, 30 parts of anhydrous glycerol, 3-parts of 2-(p-acetaminophenoxy)ethyl methacrylate, 0.2 part of ethylene dimethacrylate and 0.8 part of ethyl azobisisobutyrate was poured into a mould formed by two coplanar glass plates separated at the circumference by 1 mm thick silicon rubber tube. The mould was inserted into a water bath heated to 65°C for 5 hours. The circumferential tube was removed and the mould with the copolymer was left 20 hours in water. Then it was dismantled without difficulty and the copolymer foil was separated from the glass plates. The foil was clear and colourless after washing with glycerol and an equilibrium swelling in water. When the foil had been left for only 10 hours in 2.5N hydrochloric acid, the gel contained free aromatic amino groups, which could be proved by diazotizing with nitrous acid and coupling with resorcinol.

EXAMPLE 4

A solution consisting of 8 parts of 2-hydroxyethyl methacrylate, 2 parts of ethylene dimethacrylate, 1 part of m-acetaminophenyl methacrylate and 1 part of dibenzoyl peroxide in 100 parts of toluene was heated to boil. After 5 hours, the copolymer separated in a form of fine white globules was sucked off. To saponify the amide groups, the polymer was dispersed in 2% sodium hydroxide, heated to boiling for 2 hours and then washed with water to the loss of alkaline reaction.

EXAMPLE 5

A mixture consisting of 2 weight parts of p-acetaminophenyl methacrylate, 32 weight parts of ethylene dimethacrylate and 48 weight parts of 2-hydroxyethyl methacrylate was polymerized in suspension in 600 weight parts of water in the presence of 9.8 weight

parts of laurylalcohol and 98 weight parts of cyclohexanol. The initiator was 0.8 weight part of 2,2'-azobisisobutyronitrile. The polymerization proceeded at 70°C for 12 hours. The resulting polymer was washed with methanol and water, and hydrolyzed with 3% NaOH solution at 100°C for 3 hours. The polymer was several times washed to the loss of alkaline reaction, dried at 40°C and fractionated on screens according to the particle size.

EXAMPLE 6

A mixture consisting of 33.5 weight parts of 2-hydroxyethyl methacrylate, 32 weight parts of ethylene dimethacrylate, and 16 weight parts of 2-(p-acetaminophenoxy)ethyl acrylate was polymerized in suspension similarly as in Example 5. The hydrolysis was carried out in 5% KOH at 100°C for 1 hour. The resulting polymer was characterized by pore distribution, inner surface area and reactivity of free amino groups.

EXAMPLE 7

A mixture consisting of 38 weight parts of 2-hydroxyethyl acrylate, 32 weight parts of ethylene dimethacrylate and 12 weight parts of 2-(p-acetaminophenoxy)ethyl acrylate was polymerized in bulk in the presence of 1 weight part of dibenzoyl peroxide and 70 weight parts of dibutylether at 70°C in a cylindrical mould. The resulting polymer was hydrolyzed similarly as in Example 5.

EXAMPLE 8

The polymerization was carried out analogously as in Example 5, with the difference that 35 weight parts of divinylbenzene was used as a crosslinking monomer instead of ethylene dimethacrylate. The polymer was worked out similarly as in Example 5.

WHAT WE CLAIM IS:—

1. A method for producing a polymer which contains primary aromatic amino groups, wherein a monomer of a general formula I:

$$R^2\text{—NH—Ar}[\text{—O—CH}_2\text{—CH}_2]_x\text{—O—CO—}\underset{\substack{|\\ R^1}}{C}\text{=CH}_2$$

where R^1=H or CH_3, Ar is a bivalent aromatic residue R^2 is acyl, carboxyalkyl or sulphonyl group and x is 0 to 20 polymerized alone or copolymerized with a co-monomer which is selected from: acrylic or methacrylic acid or a compound derived therefrom; styrene or its derivatives; butadiene; isoprene; or with a mixture of two or more of these monomers, and the polymer is subsequently subjected to the elimination of the R^2 group by reaction with an acid or base resulting in the formation of an unsubstituted aromatic amino group in the side chain of the polymer.

2. A method according to claim 1, wherein the comonomer is a hydrophilic ester of acrylic or methacrylic acid containing one or more free hydroxy groups in its alcohol residue.

3. A method according to claim 1, wherein the comonomer is an N-substituted or unsubstituted amide of acrylic or methacrylic acid.

4. A method according to claims 2 or 3, wherein the copolymerization is carried out in the presence of a crosslinking monomer selected from an ester or an N-substituted or unsubstituted amide of acrylic or methacrylic acid, which contains two or more acryloyl or methacryloyl groups in its molecule; or divinyl benzene.

5. A method according to any one of claims 1 to 4, wherein the polymerization is carried out in the presence of a polymer solvent or precipitant.

6. A method according to any one of claims 1 to 5, wherein the polymerization is carried out in suspension using water as the dispersion phase.

7. A method for producing polymers which contain primary aromatic amino groups, substantially as described with reference to any one of the Examples disclosed herein.

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